# Uranium-Series Dating of Speleothems as a Means of Determining Global Paleoclimates

by

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# Abstract

770 speleothem dates were collected, and the probability of speleothem growth over time was calculated by fitting a normal distribution to each date, using the one sigma standard deviation. The distribution of recovered speleothem samples approximates an exponential curve, but it is not a simple function. By distinguishing between base dates and top dates and comparing them, glacial periods can be distinctly identified. Thirteen glacial and interglacial stages were recognized in the last 350,000 years. Despite the difference in number from the nine stages of the deep-sea oxygen isotope record, the curves are similar, and the two chronologies are mutually reaffirming.

# Acknowledgements

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# Chapter 1 Introduction

Speleothems probably provide the most continuous record that is available of continental Pleistocene chronology, because they are not subjected to dynamic surface processes. Speleothems are dated by means of uranium-series dating, which has a resolution limit of 350,000 years ago. Thus, uranium-series dating fills an important gap between the resolution of radio carbon dating (up to 50,000 years ago) and the resolution of argon fission track dating (older than 500,000 years ago).

With an increasing number of speleothems being dated, a large data set is accumulating, which will provide for more statistically meaningful results on a global scale. In this study, the data set is analyzed with the use of three variables: geographic (climatic) region, level of contamination, and the position of the sample on the speleothem.

# Chapter 2 Pleistocene Chronology

The Pleistocene epoch is characterized by alternating glacial and interglacial periods, but the chronology of the ice ages (their frequency, duration and absolute dates) is very poorly known.

A classical sequence of glacial and interglacial stages based on geomorphic evidence from glacial moraines and tills has been developed in each major glacial region (the Alps, North Europe, Britain, North America, the USSR). These classical systems recognize three to five major glacial periods. Each of these classical systems is independent and highly localized, so that there is no means of correlating between them, except for the most recent glaciation (where radio carbon dating is extensively used). Although the classical terms are still in wide use, more recent evidence suggests that the classical systems are inaccurate, and may be gross simplifications of Pleistocene chronology (as it is now thought that there were probably well over twenty glacial periods in the Pleistocene).

With the discovery of radioactivity in the early 1900's, absolute dating based on the constant decay rates of radioactive substances became possible. This has revolutionized the development of Pleistocene chronology in recent years, because radiometric dating is the only method available of calibrating events beyond the historic record to real time. It can be used to calibrate any scale of natural phenonema, such as the pollen record, calcium-carbonate-content curves, foraminiferal assemblages, the coarse-fraction record, planktonic-foraminiferal coiling scales, microfossil-assemblage changes, loesses, terraces, sealevel curves, cooling curves, and oxygen-isotope variations both in terrestrial ice and in marine sediments. The most basic of these is the binary scale of successive reversals of the earth's magnetic field. These polarity chrons have been dated with the use of K/Ar dating of terrestrial lavas. Three major magnetic boundaries that have been established are the Brunhes/Matuyama at 0.7my, the Matuyama/Gauss at 2.47my +/- 0.04my, and the Gauss/Gilbert at 3.4my. There are also intervening polarity events such as the Jaramillo event at about 0.9my (within the Matuyama chron).

Advances in oceanography have allowed scientists to apply radiometric dating to ridges and sediments on the ocean floor, which provide a much longer and more continuous record than any terrestrial sequences. For example, sea floor ridges have been used to determine the age and duration of magnetic events (Cox, 1969, Klitgord et al, 1975). It is assumed that the ridge is spreading at a constant rate, so that the sea floor basalts continuously record reversals of the earth's magnetic field. However, it must be realized that discontinuous spreading can occur, as well as ridge jumping, and unrecognized fracture zones. Therefore some subjectivity is involved in this method in choosing ridges which seem ideally continuous.

Cores of marine sediments are used in oxygen-isotope studies, as a continuous record of the changing isotopic composition of the world's oceans. It is assumed that the sediments accumulate at a constant rate, so again, subjectivity is involved in selecting cores which appear ideally continuous. Emiliani (1955) was the first to divide the isotopic record into numbered stages, alternating from warm to cold periods. He postulated that the variations in the oxygen-isotope composition of the oceans is due to variations in the amount of continental ice: in cold periods, large quantities of isotopically-light water are stored in the continental ice sheets, so that the oceans have heavy oxygen-isotope values; whereas in the warm periods the oceans have lighter oxygen-isotope values. Shackleton and Opdyke (1973) were the first to calibrate the oxygen-isotope record with the paleomagnetic record, to provide a timeframe for the numbered isotope stages. They extended Emiliani's record to 23 stages. Stage 5 is divided into 5 substages, and Stage 7 is divided into 3 substages.

The odd-numbered stages are thought to represent warm or interglacial periods, and the even-numbered stages to represent cold or glacial periods. The Brunhes/Matuyama magnetic reversal boundary is found between Stages 19 and 20, and the Jaramillo magnetic event is found at Stage 23.

Van Donk (1976) extended the record to 41 stages, but Shackleton and Opdyke (1976) considered that pre-Jaramillo isotopic fluctuations were substantially less useful as a stratigraphic tool, because they were of higher frequency and lower amplitude. Future work on cores with high rates of sedimentation may enable the system to be extended.

Piston core V28-238 (with which Shackleton and Opdyke produced their 23 stages) from the equatorial Pacific ocean provides the current definitive chronology of the Pleistocene, because of its ideal continuity and global extent. The core is widely used as a standard with which to compare other records. Kukla (1978) for example, correlated the four glacials of the classical Alpine and North-European systems with this oxygen-isotope record, using loess sections and terraces as a link. He found that the Alpine stages considered to be glacial do not correspond with the oxygen-isotope record, and concluded that the so-called Alpine interglacial stages probably represent intervals of accelerated crustal movements, rather than episodes of interglacial climate. Also, the North-European classical system is based on misinterpreted physical evidence, with lengthy gaps in the record. Thus, Kukla recommends that future subdivision of the Pleistocene be based upon continuous sequences such as those in the oceans or lakes.

However, Mix and Ruddiman (1984) assert that the oxygen-isotope record should not be used as a direct proxy for global ice volume, because the relationship is probably nonlinear. The oxygen-isotope record may misrepresent the true amplitude of the ice-volume signal. Furthermore, there is a lag time between true ice volume and the oxygen-isotope response of 1000 to 3000 years. Berggren et al. (1980) also state that there is a lag time in the order of 1000 years, to allow for the mixing of ocean waters.

Moreover, the oceanic record may not be representative of terrestrial paleoclimates and glacial events, and it is these which are most relevant and interesting to mankind. Speleothems, which form in caves, are much more representative of terrestrial processes than the oceanic record is. Since speleothems grow underground, they are not subjected to the dynamic and discontinuous processes which operate at very short time scales on the earth's surface. Caves are the most enduring element of the terrestrial landscape. Therefore, it can be expected that the speleothem record is the most continuous record of any which represent terrestrial paleoclimates. Speleothem dating may well be the most useful tool available for developing a terrestrial Pleistocene chronology.

## Chapter 3    Uranium-Series Dating of Speleothems

A speleothem is any kind of calcite precipitate which forms inside a cave. The calcite is precipitated from supersaturated groundwater by out-gassing of carbon dioxide, or by evaporation. Evaporation, however, is only responsible for speleothem formation where the relative humidity is low, such as at cave entrances or in desert caves.

Many different morphological forms of speleothems are known, but the most common are stalactites, stalagmites, and flowstone. Drips from the cave ceiling deposit hollow straws of calcite, which are stalactites. If the straw becomes blocked, the stalactite will thicken and form a conical shape. Stalagmites are usually thicker than stalactites because they grow by water splashing on the cave floor, thus producing more outward deposition. Flowstones, as the name suggests, are laminated deposits formed by water flowing down walls or along floors. Stalagmites are more amenable to dating than are stalactites because they are broader and there is no hole in the middle.

A speleothem may be "active" (in the process of formation), or it may be in a state of chemical erosion by aggressive dripwaters, or it may be completely inactive.

Speleothems are always oldest at the base, and youngest at the top. The base of a speleothem represents the initiation of its growth, and the top represents its cessation.

In order to be dated by uranium-series methods, a speleothem must have a moderate concentration of uranium. Currently, concentrations down to about 0.1 ppm U can be detected and extracted.

Uranium, like all radioactive substances, is physically unstable. The uranium isotope U234 decays into the thorium isotope Th230. U234 has a half life of about 245,000 years, which means that 245,000 years after its deposition, half of the original uranium will have decayed into thorium.

Normally, thorium would not be incorporated in a speleothem at the time of deposition, because thorium is almost completely insoluble at pH 7-8 (the normal pH of groundwater). Therefore, any thorium which is found in a speleothem must be due to radioactive decay from uranium. Since the decay rate is constant, the age of a speleothem can be calculated by measuring the accumulation of the "daughter product" thorium.

However, contamination of speleothems does occur, when clay or sand deposits are found within a speleothem. Clays are rich in Th230 and Th232. The Th230/Th232 ratio is used as a measure of contamination. At the McMaster laboratory, if a sample has a Th/Th ratio of less than 20 then the age is adjusted to account for the contamination.

In order to produce precise uranium-series dates, the speleothem must have been a closed system during and since its growth. If any uranium is lost (leached out) or added (recrystallized) then the speleothem is not appropriate for dating purposes. Massive crystalline deposits, without holes or erosion surfaces, give good results.

# Chapter 4 Literature Review

The first attempt to apply uranium-series dating to speleothems, by Rosholt and Antal (1962), concluded that speleothems were unsuitable for this dating method. They dated eight samples from several European and South African caves. They inferred that uranium loss occurred sometime after deposition, because excess Th230 and Pa231 were found in all samples. However, Cherdyntsev (1971) later pointed out that it was more likely that the determinations of uranium concentration were erroneously low.

Cherdyntsev et al. (1965) dated four speleothems from Akhshtyr Cave in Krasnodar, USSR, using Th230/U238 ratios. Although three of the speleothems were contaminated with thorium, Cherdyntsev successfully obtained similar ages for each without correction for thorium contamination.

The Th230/U234 method was used by Komura and Sakanoue (1967) on four samples from a Japanese speleothem. They determined that the growth rate between the four samples was very fast, but could not determine precise ages due to low uranium content and high thorium contamination.

Italian speleothems were dated by Fornaca-Rinaldi (1968). He erroneously equated the Th230/Th234 ratio with the Th230/U234 ratio (which is only true in the rare circumstance when the original U234/U238 ratio equals zero). This assumption would make his calculated ages significantly older than their true values.

Duplessy, Labeyrie, Lalou, and Nguyen (1970) were the first to combine uranium-series dating of speleothems with stable isotope analysis. They used five samples along a growth axis on a speleothem from Aven d'Orgnac, France. Although the sample had a very low uranium concentration, amazingly good results were obtained. The determined ages were all in correct stratigraphic sequence, and had very low error margins.

Cherdyntsev (1971) continued his studies on speleothem dating, concentrating on the problem of thorium contamination. Most of his samples, from Soviet caves, were heavily contaminated. Cherdyntsev (1971) tried to account for this contamination by extrapolating original Th230/Th232 ratios from adjacent modern deposits, assuming that the ratio stays constant over time and space.

Thompson (1973) applied isotopic analysis to speleothems from West Virginia with excellent results, clearly demonstrating the validity of Th/U dating of speleothems. Following this groundwork, Harmon (1975) analyzed 89 speleothems from Mexico, Texas, Bermuda, Kentucky, West Virginia, Iowa, the Canadian Rocky Mountains and the Northwest Territories. He applied these dates to a study of paleoclimates of North America.

For the last decade, then, speleothem dating has been increasing. The reliability of the age determinations has vastly improved over the early work (prior to 1973). A great many of the speleothem dates have been used in regional paleoclimate studies. Much of the dating work has gone on at the McMaster laboratory. Thompson (1973), Harmon (1975), and Gascoyne (1980) all wrote Ph.D.'s at McMaster on some aspect of speleothem dating.

Hennig et al. (1983) were the first to attempt a global analysis of paleoclimates using speleothem dates. They collected 480 published speleothem dates, and used an additional 184 from Hennig's own laboratory. However, the data set which they collected was very poor. Several "early" dates were used, which are considered unreliable. Also, Hennig et al. used imprecise ages (such as "less than 4,000 years old"). Furthermore, they did not have the standard deviations for many of the dates which they collected, and so they chose arbitrary standard deviations which were proportional to the date itself (whereas the standard deviations should be based on counting error, and should not be dependent on the age value itself). Indeed, 123 of the dates which Hennig et al. collected came from the visual assessment of one graph (Gascoyne, M., 1981). The actual data is not given in this reference, and Hennig et al. lists this data in categories of 5000 years, rather than listing individual dates. Moreover, Hennig et al. tend to use non-corrected contaminated ages, which gives a bias towards older dates (a contaminated sample will produce a date which is older than its real age).

Hennig et al. produced a frequency curve of "error-weighted ages" to account for standard deviation. Figure 1 shows both the original histogram and the final frequency curve. They converted the histogram by making the height of each age rectangle equal to the age divided by the sum of the total one sigma standard deviation. This formula has the effect of making larger dates (older speleothems) more significant than younger dates. In the original histogram, the abundance of very young speleothems is obvious, but Hennig et al. distort this by asserting that the greatest abundance of speleothem growth was 98,000 years ago (according to their weighted error calculations).

Uranium-series dating of speleothems has a great deal of potential in determining global paleoclimates, but care must be taken to use a good data set, and to use a more accurate method of portraying the standard deviations of each date.

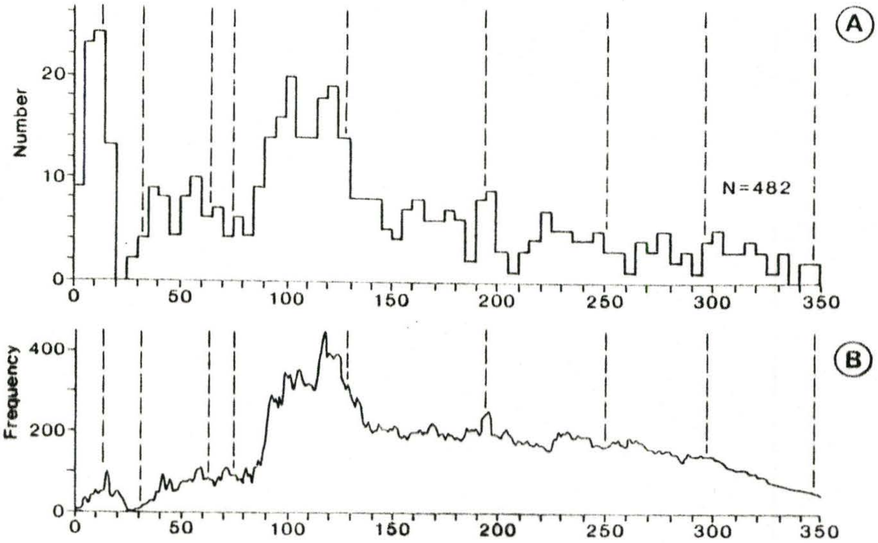

Figure 1 Error weighting of speleothem frequencies (from Hennig et al., 1983)

# Chapter 5

# Theoretical Expected Distribution

## A. Speleothem Growth

Speleothem growth depends on a continuous flow of water into an air-filled passageway. If the cave passage floods, no growth can occur at all. The rate of growth, however, depends both on the rate of water flow and on the difference between the concentration of carbon dioxide in the percolation water and the cave atmosphere respectively. These factors may be considered on a very small scale (rates of speleothem growth vary within a cave system and even within a cave passage or chamber), or on a global scale. Thus, the rate of speleothem growth will decrease with increasing aridity, and also with decreasing available carbon dioxide. High concentrations of carbon dioxide in groundwater are largely the result of organic activity in the soil, which decreases in cold or glacial periods. Therefore, the rate of speleothem growth in glacial or periglacial areas should tend to decrease during glacial periods.

Flooding of cave passageways may occur locally due to high precipitation or snowmelt-induced runoff or chance blockage. Such events are temporary, and speleothem growth will resume after the end of the event. However, a thin film of mud on the surface of the speleothem will often result, with accompanying detrital thorium contamination.

Cave passages may also flood for longer periods of time. Once a cave passage is created, it may be abandoned and re-invaded several times over, with variations in the piezometric surface of the cave. Speleothem growth may be resumed after a hiatus which may last for many thousands of years. Such hiatuses are usually recognisable by a discontinuity in the growth layers due to re-solution.

Finally, a cave passage may be flooded even more permanently, by a rise in base level. This has occured in some tropical caves which are below the present sea level. If a speleothem is found in a submerged cave, it can only have grown during a glacial period when sea levels were lower (and the passage was air-filled). Therefore, the distribution of ages of tropical submarine speleothems should increase during glacial periods, in direct contrast to the distribution of ages of speleothems found in glaciated areas, which should decrease during glacial periods.

Speleothems in humid tropical areas could have grown either during glacial or interglacial periods. Since they are not directly influenced by glaciations, their rate of growth should be continuous over time. However, they may experience slight decreases in growth during glacial periods just because the climate is generally colder during these periods around the globe, and organic activity (and therefore carbon dioxide production) may decrease.

Active speleothem growth does not occur in arid areas such as New Mexico or Israel. However, many fossil speleothems exist in these areas, which must have grown under climatic conditions differing from the present. It is probable that during the ice ages, some modern arid areas were more temperate and humid. Therefore, it is theorized that the abundance of speleothems found in modern arid areas should peak during glacial periods (similar to the submarine subset).

## B. Recovered Samples

Little analysis has been done on measuring rates of speleothem growth. A determined age of a speleothem indicates that the speleothem was growing at that time, but not how fast it was growing. If rates of speleothem growth were measured, they could be used as much more direct indicators of paleoclimate. A speleothem may grow very slowly during a glacial period, but not stop altogether. Castleguard Cave in Canada, for example, is covered by a glacier yet still experiences active (albeit slow) speleothem growth. Therefore, it is possible to obtain a date of a speleothem which grew during a glacial period, although the probability is significantly less.

The probability of actually collecting speleothem samples varies with the age of the speleothem. With increasing age, a speleothem is more likely to have been buried with clastic sediment in the cave, or eroded either by aggressive chemical action of the cave waters or by mechanical abrasion by bedload. (Flowstones, which are more massive, are less susceptible to erosion or burial than are stalagmites and stalactites. Thus, one would expect the ratio of stal. to flowstone ages to decrease with age. However, this is not tested in this study). Also, the very passage within which the speleothem is found may be blocked, infilled, or eroded away at the surface. Therefore, (assuming constant climate), the theoretical expected distribution of recovered samples will decrease with time in some manner.

This decrease could be described either by an exponential curve, or as a power function. If one considers that burial and erosion events only happen in active passages (where flooding occurs, and clastic sediments are transported), then a speleothem which exists in an abandoned passage has a significantly lower chance of being eroded or buried than a speleothem which exists in an active passage.

This process would result in a power function. However, if one further considers that abandoned passages are more susceptible to extinction, then the more suitable function would be an exponential curve (where each speleothem has an equal probability of being eroded or buried). Therefore, the theoretical expected distribution of recovered samples may be either an exponential curve, a power function, or something in between. In glacial margins, abandoned glacial passages are often reactivated in glacial periods, and this is another unpredictable perturbing factor which tends to force the function away from a simple power or exponential function.

The distribution of recovered samples is also influenced by biases on the part of the samplers. If a sampler is interested in determining the age of a cave passage, he/she will sample speleothems which appear to be the oldest in the passage. Conversely, if a sampler is interested in obtaining a good clean date for paleoclimate analysis, he/she will try to sample speleothems with the least possible contamination and leaching. It is difficult to determine how these biases influence the overall distribution in large sample sets. However, such sampling bias is useful in explaining what are otherwise individual anomalies in the distribution of recovered samples (i.e. when the distribution is not adequately explained by other factors, it can probably be explained by sampling bias).

# Chapter 6 Data and Method

Hennig et al. (1983) collected 480 published speleothem dates, and used an additional 184 from his own laboratory. However, he did not have access to unpublished dates from the McMaster University laboratory, which has done (and is doing) more speleothem dating than any other laboratory in the world. The total accumulation of McMaster dates is well over 1000.

Most of the McMaster dates have been used in specific regional studies by different researchers, and until recently, little effort has been made to keep a systematic record of the total accumulation of speleothem dates. Therefore, the data had to be collected from several different sources, and continually cross-checked to prevent duplication. Furthermore, occasional discrepancies were found between ages recorded in two different sources for the same sample. Rounding-off of original ages, as well as typographical or recording errors, caused problems.

Unfortunately, due to time constraints, not all of the available data has yet been analyzed. The total data set used in this study contained about 770 dates, but approximately 90 dates were rejected because they were out of range of this study (over 350,000 years old), or because they were imprecise ages (for example, a date of "less than" 7000 years). There were also several ages rejected because they were considered unreliable or suffered from gross contamination (with negative corrected ages). Altogether, then, 679 dates are used for paleoclimate analysis in this study. This number compares to 596 used by Hennig et al. (they had 60 dates older than 350,000 years, and 8 with imprecise ages, making a grand total of 664). Both Hennig et al.'s data set and the data set used in this study show consistently that 10% of the total samples are greater than 350,000 years old, and 1% of the total samples are unsuitable due to imprecision, so that 89% of the total samples may be used for paleoclimate analysis.

Often dates are repeated for confirmation, or two different dating methods are used on the same sample (most commonly, Th/U dating is confirmed or checked by Pa/Th dating). However, since this study is measuring the occurrence of speleothem dates rather than the rate of speleothem growth, ideally only one sample should be used from each speleothem. Otherwise, the distribution is biased towards particularly interesting or problematic speleothems, which more than likely are not representative of the total population. Therefore, repetitions have been avoided in this data set, although some repetitions may in fact be included in the data set simply because they were not documented as such.

Inadequate documentation is a major problem in this study. The position of the sample on the speleothem (base or top) is very often not recorded. A great deal can be learned from comparing base and top dates, but the subsets should be bigger. A small subset of the total data set must be used, simply because of lack of information for a great many of the dates. Another problem in this regard is that almost every speleothem has a sample dated at its base, but proportionately few tops of speleothems have been dated.

Each sample in this study has three variables, along with the date and standard deviation. The variables are: its geographical region, its position on the speleothem, and whether or not it is contaminated. The data for each of the variables is categorical (e.g. a given sample may be either glacial or periglacial, top or base, contaminated or non-contaminated), rather than using integral values for each variable.

The samples were placed in geographical sub-regions, which were then grouped into regions. Canada, Minnesota, Ireland, Norway, Poland, Yorkshire and Austria were classified as glacial; West Virginia, Mendips, Czechoslovakia, France, Yugoslavia, Spain, Germany and Italy were classified as periglacial; Belize, China, Greece, Israel, Mexico, Turkey, South Africa and Carlsbad Caverns, New Mexico) were classified as tropical; and Bahamas and Bermuda were classified as tropical submarine. Not all sub-regions had a homogeneous paleoclimate, however. For example, some sites in France were periglacial and some were glacial. Again due to limited documentation, it would be a very onerous task to determine whether the site of each individual date was glaciated or not. Therefore, since most caves in France would be in periglacial areas, France has been classified as a periglacial area. Similar "lumping" has been done for each region.

In this study, any sample with a Th/Th ratio less than 20 is considered contaminated. The McMaster dating program produces a corrected (or "adjusted") age for any sample with a Th/Th ratio below this level. Other technical difficulties, such as low uranium content or low chemical yields of uranium or thorium, were not considered in this study, as they are of minimal importance.

A Fortran program (CORKSCREW) was written to produce curves showing the probability of speleothem growth over time. A normal distribution was fitted to each sample (using the date and standard deviation of each sample as parameters), and then the probability distributions of individual samples were added together, to produce the total probability of speleothem growth over time (in units of one thousand years).

Subsets for each different geographical region can be entered separately into the program. Furthermore, two modifications of the program were produced: one which uses the entire subset (CORK), and one which uses only the non-contaminated samples of the subset (SCREW). SCREW can be further modified to use only top dates, only base dates, only middle dates, only bulk dates, only dates for which the position on the speleothem is unknown, or any combination of the above. The program CORK is shown in Appendix One, and SCREW is shown in Appendix Two.

# Chapter 7 Results

Figure 2 shows various graphical presentations of the data set. On each graph, time (in thousands of years before the present) is shown on the x axis, and probability of speleothem growth is shown on the y axis (where probability is calculated by fitting a normal curve to each date using the one sigma standard deviation). The data is presented as linear, as semi-log with the log scale on the y axis (log-linear), as semi-log with the log scale on the x axis (linear-log), and as log-log.

The linear graph shows clearly that there is an abundance of speleothems which are younger than approximately 15,000 years. The probability of speleothem growth then drops off dramatically (to less than 25%), in a trend which is similar to an exponential curve. Fluctuations between 20,000 years ago and 150,000 years ago are assumed to represent glacial and interglacial periods, but the graph evens out after 150,000 B.P., as the resolution of the dating process declines.

If the line were straight on the log-linear graph, it would mean that the probability of speleothem growth was an exponential function. Even allowing for glacially-induced perturbations in the line, the line is not quite straight, but it closer to being straight than any other line on any of the other graphs. Therefore, the function is closer to an exponential curve than any other kind of relationship.

The advantage of the linear-log is that the recent end of the time scale is spread out, and the latter end of the time scale is compressed. Thus, more detail is shown of the younger speleothems, which are more abundant, and less importance is attached to the older speleothems, which have less resolution in the dating process. The greater detail of the younger speleothems illustrates clearly, for example, that samplers tend not to collect active speleothems, so that speleothems less than 3,000 years old are less abundant. Despite these advantages, however, this type of graphical presentation does not clearly show a line or general trend of speleothem growth, and the log-linear plot is preferable for this reason.

If the line on the log-log plot were straight, then the probability of speleothem survival would be a power function. But the line is clearly not straight, and therefore, again, the log-linear graph is preferable (because it is closer to a straight line). It could be argued, however, that the log-log would in fact show a straight line if an adjustment was made to account for the fact that significantly less speleothems have been sampled younger than 3,000 years old. However, for purposes of presentation, the remaining results will be presented on semi-log graphs with the log scale on the y axis because this presentation best approximates a straight line.

Figure 3 shows the results by geographical regions. The total data set is compared to the glacial subset, the glacial subset is compared to the periglacial subset, the glacial subset is compared to the tropical subset, and the glacial subset is compared to the submarine subset.

The glacial subset clearly has a large influence on the total data set, because the trends of both lines are similar. This is logical because the glacial subset is almost half of the total data set (300 out of 679 dates).

The comparison of the glacial subset and the periglacial subset, shows some interesting results. Both subsets show a marked decrease in speleothem growth in the last glaciation (approximately 30,000 years ago). However, the glacial subset also indicates a major glaciation approximately 85,000 years ago, but there is no indication of this whatsoever in the periglacial subset. Therefore, it may be concluded that the glaciation 85,000 years ago was cold enough to stop speleothem growth in glacial areas, but was not cold enough to affect speleothem growth in the sampled periglacial areas. Similarly, the glacial subset shows probable cold periods at about 155,000 years ago and at 225,000 years ago, which are not indicated by the periglacial subset.

The glacial subset is compared with the tropical subset. Especially in the last 100,000 years, there seems to be a tendency for increases in speleothem growth in the tropical subset to coincide with decreases in speleothem growth in the glacial subset. For example, during the two coldest glaciations indicated by the glacial subset (30,000 years ago and 85,000 years ago) there is an increase in speleothem growth in the tropical subset. This gives credence to the theory that many tropical areas which are arid in modern times were actually temperate and humid during glacial periods, so that speleothem growth increased in these areas during ice ages. The trend could possibly be seen more clearly if the tropical "wet" dates (such as Mexico and Belize) could be separated from the tropical "arid" dates (such as Israel and Carlsbad Caverns, New Mexico). However, the data set is simply too small to allow for this. The tropical subset contains only 49 dates, and less than ten of these can be definitely classified as arid in modern times, and a data set of that size would not give accurate results.

The size of the data set is also a problem in the tropical submarine subset. The tropical submarine subset consists of only 25 samples, which is not big enough to accurately represent the total population of tropical submarine speleothems. The fact remains, however, that submarine speleothems could have formed only when sea levels were low enough to leave an air-filled passage; and sea levels were lowered in cold or glacial periods. Thus, it is expected that increases in speleothem growth in the submarine subset will coincide with decreases in speleothem growth in the glacial subset. This does in fact occur in the last glaciation (30,000 years ago). Also, there is a marked decrease in speleothem growth in the submarine subset approximately 60,000 years ago, which corresponds to a relatively warm period according to the glacial subset. It appears, therefore, that the theory is confirmed, but it should be tested with a larger subset.

Figure 5 compares the total data set with the total non-contaminated data set (where any date with a Th/Th ratio less than 20 is considered contaminated). It can be seen that the two lines follow the same trends or distribution, so that it can be argued that contaminated dates do not misrepresent the total distribution. However, it can also be seen that the non-contaminated subset shows glacial and interglacial stages much more distinctly. The amplitude of the last glaciation (30,000 years ago) is much larger in the non-contaminated subset; in fact it is twice as large as that shown by the total data set. Therefore, the non-contaminated data set is preferable because it shows much clearer results.

Figure 6 shows the results by position on the speleothem. The samples were divided into base and top dates. A subset of "bases only" has two advantages in terms of accuracy. Firstly, it means that only one date per speleothem is used, and so reduces the bias caused by speleothems which have had several dates taken along their axes. Secondly, it means that each date in the subset specifically represents the initiation of speleothem growth, rather than simply the occurrence of speleothem growth. Therefore, an increase in the number of speleothem base dates is more likely to indicate the beginning of a warm period, rather than just any point in the duration of a warm period. A comparison of all the bases with the total data set (see Figure 6) shows clearly that the subset of bases gives a much more distinct representation of glacial and interglacial periods than does the total data set. The amplitude of the last glaciation is an entire order of magnitude larger in the bases subset than in the total data set. This is due to the elimination of multiple dates from the same speleothem, and the effect is similar to eliminating contaminated dates. Furthermore, the effect of representing only the beginning of interglacial periods can also be seen. The bases subset shows a peak at 120,000 years ago, whereas the total data set shows a peak plateau from 100,000 years ago to 120,000 years ago. A comparison of the glacial subset with the glacial bases shows a similar pattern. The graph of glacial bases and all of the bases does not show the same correspondence shown between the entire glacial subset and the total data set seen above. The bases of the total data set show a warm period at approximately 25,000 years ago which is not indicated by the bases of the glacial subset; also, the bases of the glacial subset show a glacial period (in fact the lowest trough in the chronology) which is only hinted at by the total data set.

A juxtaposition of all of the base dates against all of the top dates gives a very clear portrayal of the start and finish of glacial periods. A peak of base dates suggests the beginning of an interglacial period, and a peak of top dates suggests the beginning of a glacial period. From the graph, then, a Pleistocene chronology can be developed as follows: interglacial conditions from the present to 15,000 years ago, and previous interglacials between 25,000 and 30,000; 45,000 and 65,000 (with three small cold periods within it); 95,000 and 130,000; 170,000 and 200,000; 210,000 to 255,000 years ago, and finally 275,000 and 350,000 years ago (the limit of resolution).

This chronology correlates very well with the deep-sea oxygen-isotope chronology. Figure 7 shows the isotope record in comparison to the entire data set as well as the glacial bases subset.

The isotope record subdivides the last 350,000 years into 9 stages, whereas the data from this study (Figure 6.4) suggests 13 stages. However, if the 13 stages from this study are correlated to the fluctuations on the isotope record (rather than simply looking at the stage boundaries), it can be seen that there is excellent correlation.

Figure 7 shows that the glacial bases subset correlates to Shackleton and Opdyke's data much better than the total data set does. As discussed earlier, it has greater amplitude, and thus shows the glacial stages more clearly.

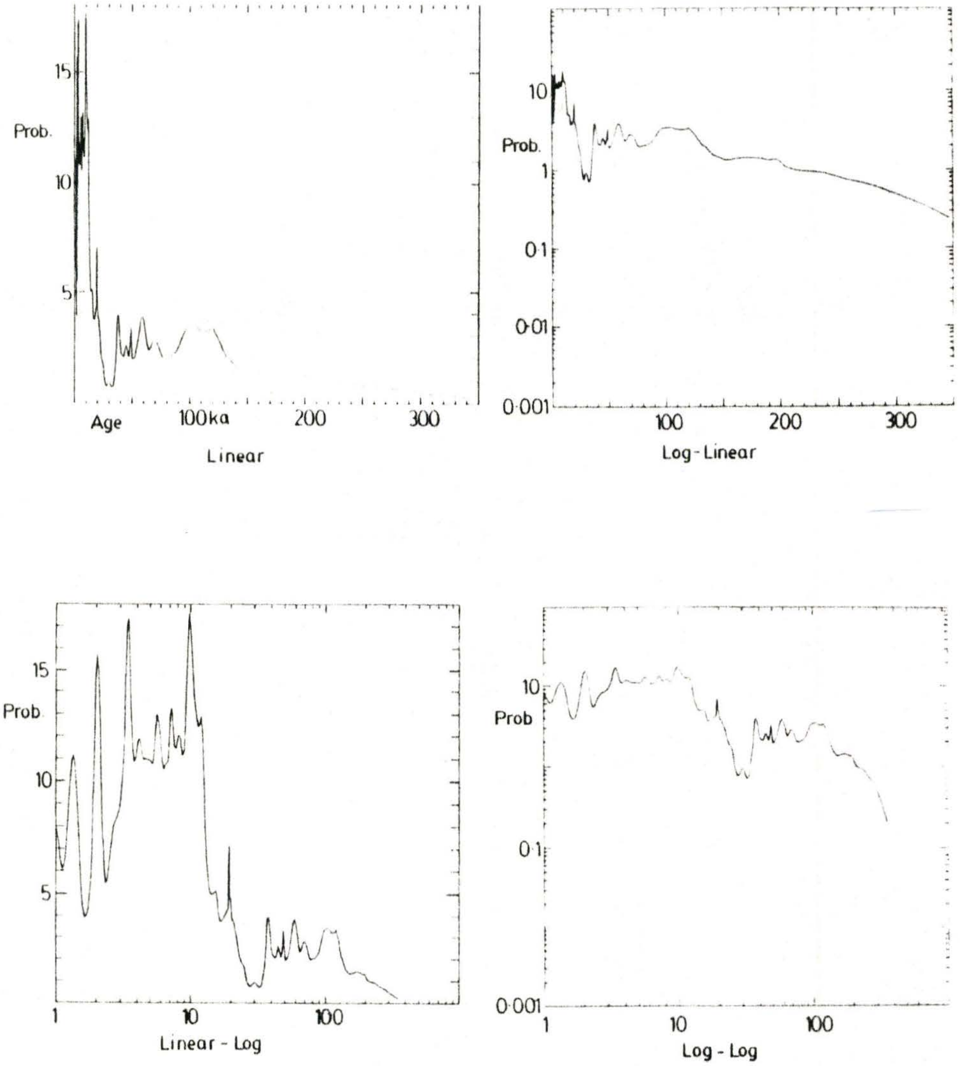

Figure 2 Graphical presentation of speleothem frequencies

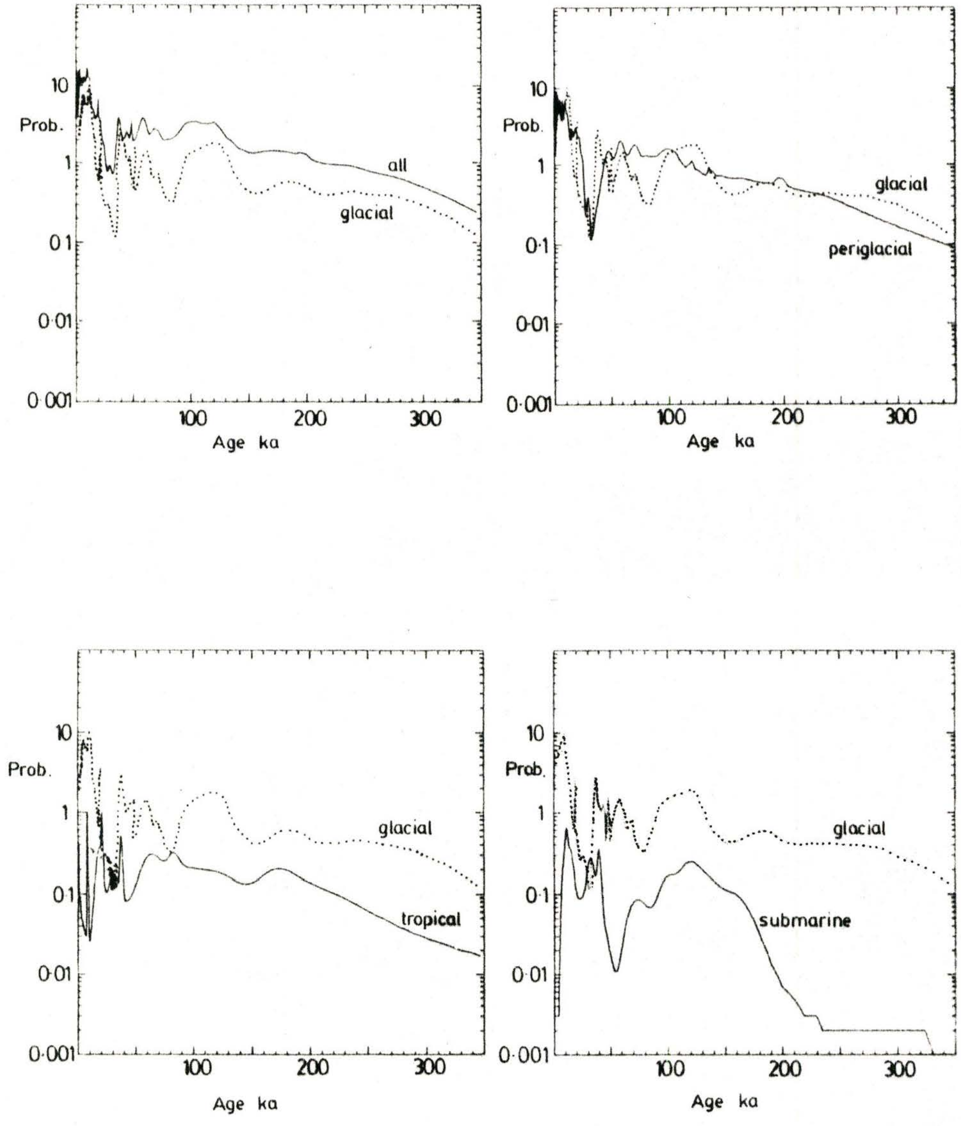

Figure 3 Speleothem frequencies by geographical region.

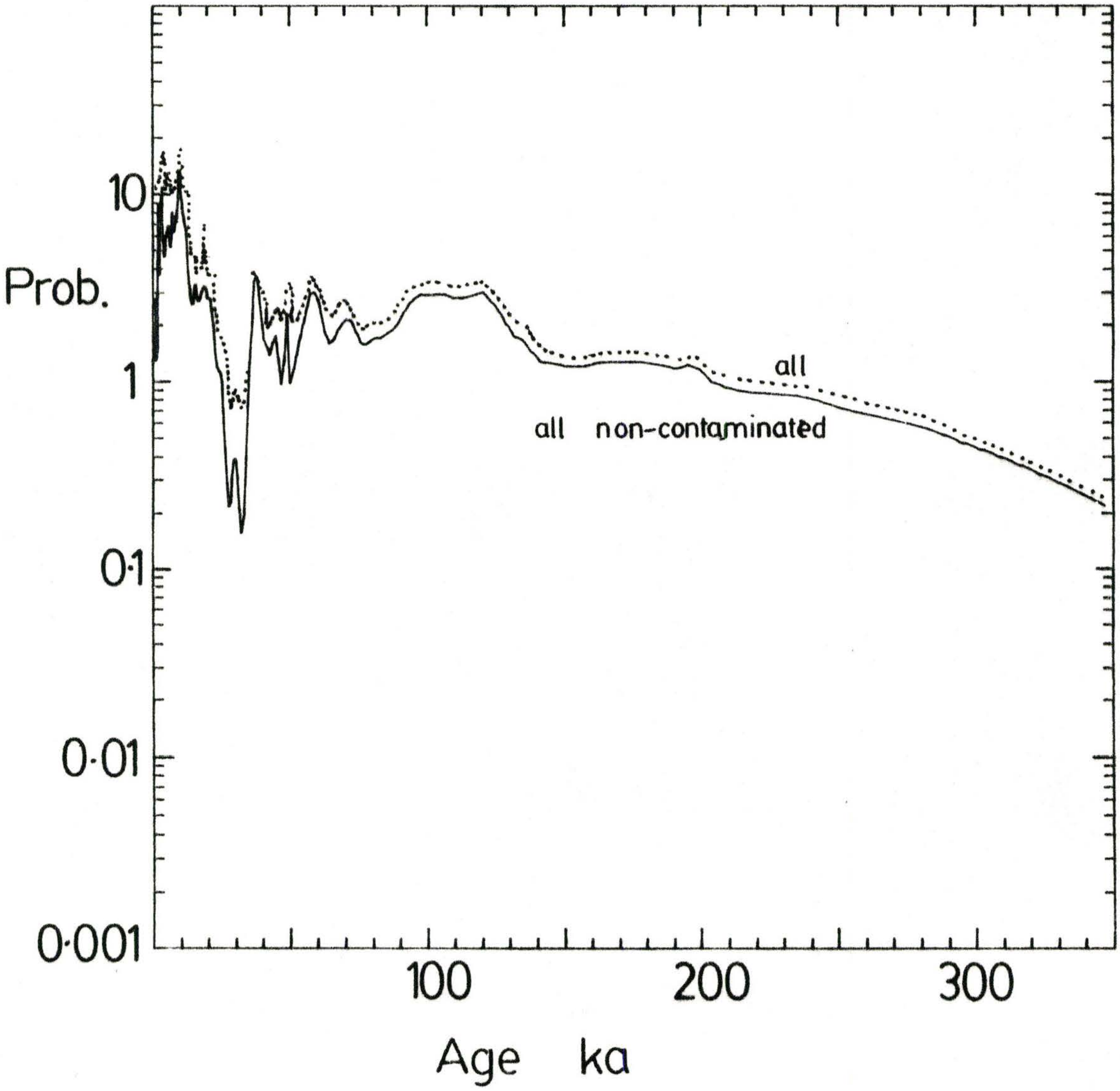

Figure 4 Speleothem frequencies: the effect of contamination.

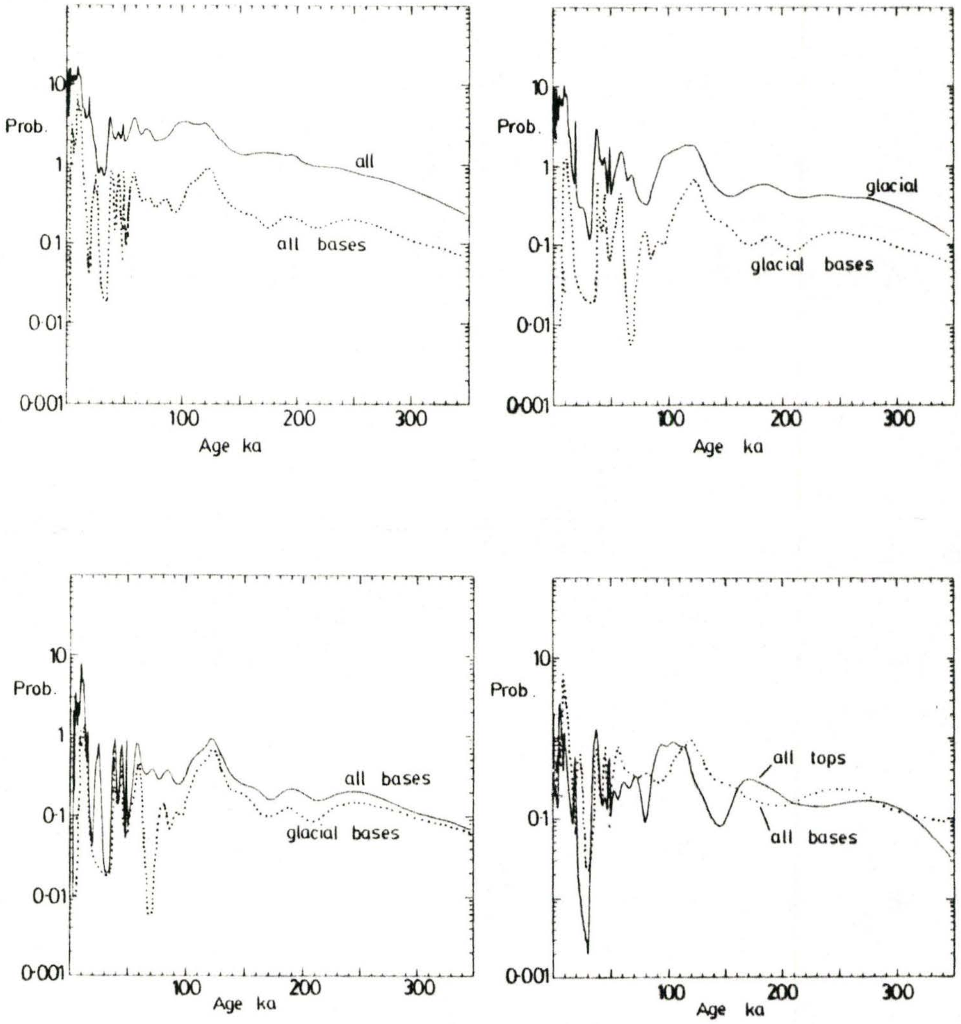

Figure 5 Speleothem frequencies: bases and tops of samples.

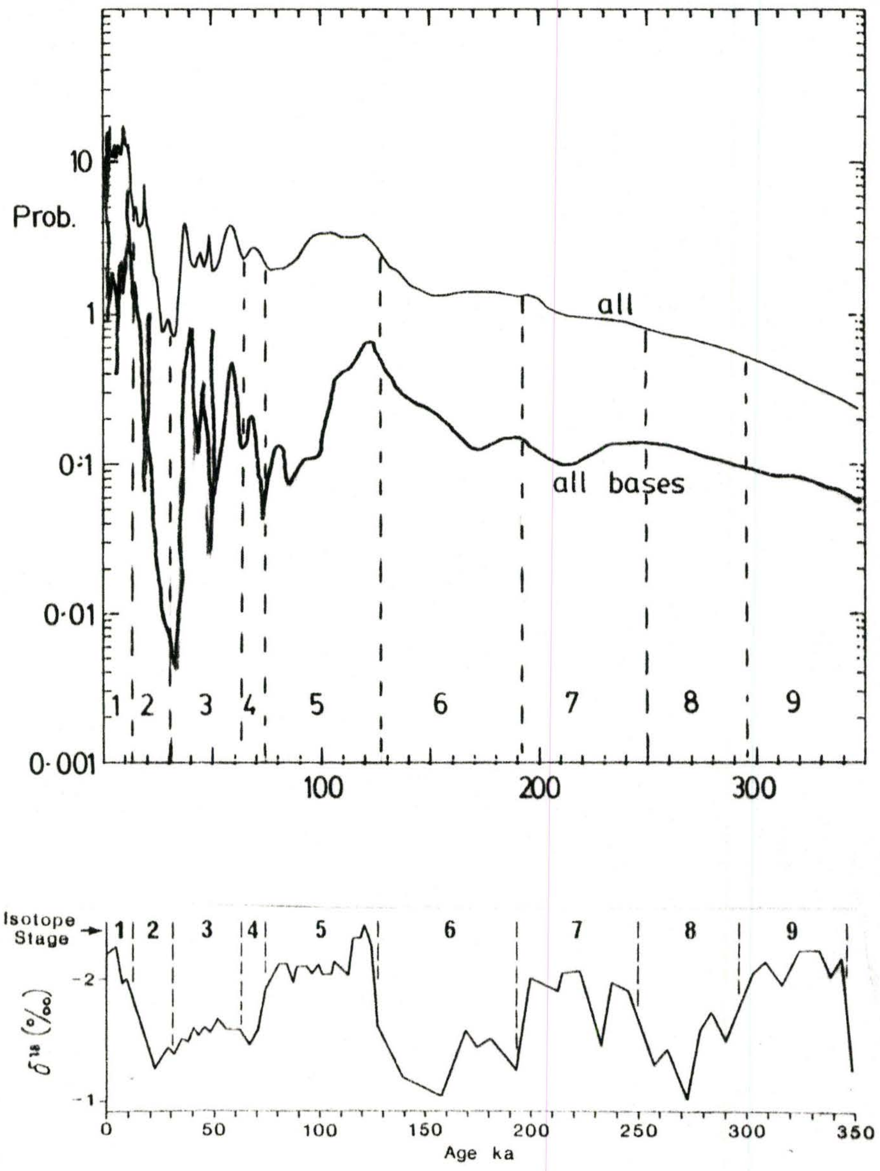

Figure 6 Correlation of speleothem and Oxygen isotope chronologies (from Shackleton et al., 1976).

## Chapter 8 Conclusion

Uranium-series dating of speleothems is a valid, reliable, and accurate method of determining global paleoclimates. For best results, it is necessary to eliminate contaminated and other questionable dates, and to separate the data into geo-climatic regions, and to contrast base dates against top dates. Furthermore, the data set should be as large as possible.

This study identified thirteen distinct glacial and interglacial periods in the last 350,000 years. Moreover, excellent correlation was achieved with the most widely recognized Pleistocene chronology.

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```
          PROGRAM CORK
          DIMENSION H(0:255),AGE(0:255)
          CHARACTER *15 PLACE
          DATA H/256*0.0/
          DATA AGE/256*0.0/
          OPEN (5,FILE='SUBMAR')
          OPEN (7,FILE='OUTPUT')
          READ (5,600)PLACE
          F=SQRT(0.5)
          PT=0
          DO 100 J=1,999
            READ (5,200,END=110) AVE,SD
            AVLOG=LOG10(AVE)
            AAS=LOG10(AVE+SD)
            SDLOG=(AAS-AVLOG)*100
  20        SDX3=(AAS-AVLOG)*3
            B=(AVLOG-SDX3+0.01)*100
            C=(AVLOG+SDX3+0.009)*100
            AVLOG=AVLOG*100
            Z=3
            MIN=B
            MAX=C
            IF (MIN.LT.1)MIN=1
            DO 50 KOUNT=MIN,MAX
              IF (FLOAT(KOUNT).LT.AVLOG) THEN
              ZA=(AVLOG-FLOAT(KOUNT))/SDLOG
              P=0.5*ERFC(-F*Z)-0.5*ERFC(-F*ZA)
              H(KOUNT)=H(KOUNT)+P
              Z=ZA
              PT=PT+P
              ELSE
              PA=0.5*ERFC(-F*ZA)-0.5*ERFC(-F*0.0000000001)
              ZA=(FLOAT(KOUNT)-AVLOG)/SDLOG
              PB=0.5*ERFC(-F*ZA)-0.5*ERFC(-F*0.0000000001)
              P=PA+PB
              H(KOUNT)=H(KOUNT)+P
              Z=ZA
              PT=PT+P
              KENNY=KOUNT+1
              GO TO 60
              ENDIF
       50     CONTINUE
       60   DO 80 MOUNT=KENNY,MAX
              IF (MOUNT.GT.255)GO TO 100
              ZA=(FLOAT(MOUNT)-AVLOG)/SDLOG
              P=0.5*ERFC(-F*ZA)-0.5*ERFC(-F*Z)
              H(MOUNT)=H(MOUNT)+P
              Z=ZA
              PT=PT+P
       80     CONTINUE
  100     CONTINUE
  110     WRITE (7,700) PLACE,PT,J-1
          WRITE (7,750)
          DO 130 JANE=1,255
            AGE(JANE)=10**(FLOAT(JANE)/100)
  130     CONTINUE
          DO 150 L=1,85
            FRED=(AGE(L))-(AGE(L-1))
            H(L)=H(L)/FRED
            WRITE (7,500) L,AGE(L),H(L),L+85,AGE(L+85),H(L+85),L+170,A
    +GE(L+170),H(L+170)
  150     CONTINUE
  200     FORMAT (F5.1,F7.1)
  500     FORMAT (1X,I3,F6.2,F8.3,9X,I3,F7.2,F8.3,9X,I3,F8.2,F8.3)
  600     FORMAT (A)
  700     FORMAT (1H1,A,4X,'TOTAL PROBABILITY=',F8.3,9X,'TOTAL SAMPLES
     +=',I3)
  750     FORMAT (1H0)
          END
```

```
      PROGRAM PSCREW
      DIMENSION H(0:255),AGE(0:255)
      DATA H/256*0.0/
      DATA AGE/256*0.0/
      OPEN (5,FILE='GLACIAL')
      OPEN (7,FILE='GBASES')
      F=SQRT(0.5)
      PT=0
      DO 100 J=1,999
        READ (5,200,END=110) AVE,SD,SUB,IMTB,KON
        IF (IMTB.GT.0) GO TO 100
        AVLOG=LOG10(AVE)
        AAS=LOG10(AVE+SD)
        SDLOG=(AAS-AVLOG)*100
   20   SDX3=(AAS-AVLOG)*3
        B=(AVLOG-SDX3+0.01)*100
        C=(AVLOG+SDX3+0.009)*100
        AVLOG=AVLOG*100
        Z=3
        MIN=B
        MAX=C
        IF (MIN.LT.1)MIN=1
        DO 50 KOUNT=MIN,MAX
          IF (FLOAT(KOUNT).LT.AVLOG) THEN
          ZA=(AVLOG-FLOAT(KOUNT))/SDLOG
          P=0.5*ERFC(-F*Z)-0.5*ERFC(-F*ZA)
          H(KOUNT)=H(KOUNT)+P
          Z=ZA
          PT=PT+P
          ELSE
          PA=0.5*ERFC(-F*ZA)-0.5*ERFC(-F*0.0000000001)
          ZA=(FLOAT(KOUNT)-AVLOG)/SDLOG
          PB=0,5*ERFC(-F*ZA)-0.5*ERFC(-F*0.0000000001)
          P=PA+PB
          H(KOUNT)=H(KOUNT)+P
          Z=ZA
          PT=PT+P
          KENNY=KOUNT+1
          GO TO 60
          ENDIF
   50   CONTINUE
   60 DO 80 MOUNT=KENNY,MAX
          IF (MOUNT.GT.255)GO TO 100
          ZA=(FLOAT(MOUNT)-AVLOG)/SDLOG
          P=0.5*ERFC(-F*ZA)-0.5*ERFC(-F*Z)
          H(MOUNT)=H(MOUNT)+P
          Z=ZA
          PT=PT+P
   80   CONTINUE
  100 CONTINUE
  110 DO 130 JANE=1,255
        AGE(JANE)=10**(FLOAT(JANE)/100)
  130 CONTINUE
      DO 150 L=1,255
        FRED=(AGE(L))-(AGE(L-1))
        H(L)=H(L)/FRED
        WRITE (7,500) AGE(L),H(L)
  150 CONTINUE
  200 FORMAT (F5.1,2F7.1,I5,I1)
  500 FORMAT (1X,F8.2,F8.3)
      END
```